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Task IV

Polybrominated Biphenyls

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16. ABSTRACT

The recent Michigan incident, in which livestock feed was contaminated by polybrominated biphenyls (PBBs), prompted this investigation. This report reviews the technical and commercial history of PBBs and also gives a general overview of the production, consumption and ultimate fate of these compounds. A detailed discussion of the manufacturing process and consumption patterns identifies possible points of entry of PBBs into the environment. A summary of air emissions, and the technology involved is discussed; and the ultimate disposal of liquid and solid waste material was investigated. Finally, a cost/performance analysis of alternative flame retardant is presented.

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SECTION I. STATUS OUTLOOK AND SUMMATION

I.1 TECHNICAL AND COMMERCIAL HISTORY OF POLYBROMINATED BIPHENYLS

Polybrominated biphenyls (PBBs) are industrial compounds that were used as flame retardants in various plastic materials from 1970 to 1974, about 40 years after the introduction of their chlorinated analogues, the PCBs. The PBBs produced domestically for commercial use included hexabromobiphenyl (marketed as Firemaster BP-6 by Michigan Chemicals), octabromobiphenyl and decabromobiphenyl.*

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*The polybrominated biphenyls discussed in this report refer to the commercial products.

n + m = 6 Hexabromobiphenyl
n + m = 8 Octabromobiphenyl
n + m = 10 Decabromobiphenyl

Figure 1-1. General Structure of Polybrominated Biphenyls

The bromine content of these products ranges from about 77% for Firemaster BP-6 to about 82% for the decabromobiphenyl. Several structural isomers of each of these brominated biphenyls are possible and may be present in the product. The composition of Firemaster BP-6 has been given as follows:

Hexabromobiphenyl	63%
Heptabromobiphenyl	14%
Pentabromobiphenyl	10%
Tetrabromobiphenyl	2%
Other bromobiphenyl	11%

In addition to the various PBBs present in Firemaster BP-6, the presence of brominated naphthalenes (tetrabromo to hexabromo) has also been detected (O'Keefe, 1977).

An analysis of Bromkal 80, (Norstrom, 1976) manufactured by Chemische Fabrik Kalk, Germany, showed the following composition:

Hexabromobiphenyl	1%
Heptabromobiphenyl	27%
Octabromobiphenyl	72%
Nonabromobiphenyl	Trace

Three octabromobiphenyl isomers were found to be present at 14%, 16% and 42%.

In 1973, Firemaster BP-6 was accidentally mixed with cattle feed, which, in turn, was distributed to a large number of farmers in Michigan. The extent of the hazard to the health of the Michigan farmers and consumers of dairy products has not yet been fully evaluated, but the livelihood of hundreds of farmers has been disrupted and thousands of farm animals have been quarantined and destroyed (Hecht, 1977; Chem. Eng. News, 1975).

It is against this background that considerable interest in PBBs has been aroused among environmental chemists and biologists. This interest is based on both the severe accidental poisoning described above, and the structural similarity of PBBs to the well known pollutants polychlorinated biphenyls (PCBs). The purpose of this study, undertaken for the Office of Toxic Substances of the Environmental Protection Agency, was to define the routes and sites through which the chemical is entering the environment.

1.1.1 Manufacturing History

During the period 1970 to 1976, approximately 13.3 million pounds of polybrominated biphenyls were produced in the U.S. About 11.8 million pounds of this total were Firemaster BP-6 and FF-1, the remaining 1.5 million pounds consisted of octabromobiphenyl and decabromobiphenyl. The sole U.S. producer of hexabromobiphenyl, Michigan Chemical Company (now Velsicol), St. Louis, Michigan, ceased production in November, 1974, at the request of the State of Michigan. Their inventory was exhausted in April, 1975 (McDonald, 1977). All companies with the potential to produce the hexabrominated biphenyl consider it to be too toxic to do so.

Two producers have continued to manufacture octabromobiphenyl and decabromobiphenyl since 1974. They are White Chemical Company, at Bayonne, N.J., and Fine Organics Division of Hexel Corporation, at Bayreville, N. J.

The estimated total production of polybrominated biphenyls in the U.S. for the period 1970 to 1976 is shown in Table 1-1. Available data indicate that PBBs were not produced on a commercial basis prior to 1970.

TABLE I-1. TOTAL COMMERCIAL DOMESTIC PRODUCTION OF POLYBROMINATED BIPHENYLS, 1970-1976

(Industry Sources, 1977)

PRODUCT / ESTIMATED MIXTURE BY YEAR	1970	1971	1972	1973	1974	1975	1976	ESTIMATED TOTAL
Hexabromobiphenyl	20,900	185,000	2,721,000	3,887,000	4,867,000	0	0	Totals 11,347,900
Octabromobiphenyl and Decabromobiphenyl*	31,000	31,000	32,000	359,000	136,000	170,000	805,000	Totals 1,538,000
Estimated Total U.S. Production of Polybrominated Biphenyls	51,900	216,000	2,753,000	4,248,000	4,988,000	170,000	805,000	Totals 12,731,900

* These figures represent mainly the decabromobiphenyl. Truck load quantities (less than 40,000 pounds) of the octabromobiphenyl may have been produced in 1970, 1971, 1972, 1975 and 1976).

During 1971 and early 1972, a small amount of a developmental product Firemaster FF-1 was produced by Michigan Chemical: 15,000 pounds in 1971 and 131,000 pounds in 1972. This material was ground Firemaster BP-6 containing 2% by weight of an anticake agent. Firemaster FF-1 was prepared by shipping BP-6 to Cincinnati Chemical Processing Company, Batavia, Ohio, where it was ground and blended then shipped directly to customers, or returned to Michigan Chemical Corporation's St. Louis plant.

The process for manufacturing PBBs is a general process that can be applied to the bromination of a number of organic hydrocarbons. It consists of a Friedel-Crafts type reaction wherein biphenyl is reacted with bromine in the presence of chloride in an organic solvent, using an aluminum chloride catalyst.

The air emissions from Michigan Chemical's hexabromobiphenyl operation were controlled by a spot ventilation system with localized ventilation from various process areas, two absorber vents, and ambient air in the general process area.

A survey conducted in May, 1974, at Michigan Chemical Co. indicated hexabromobiphenyl concentrations of 3×10^{-6} mg/l at the spot vent and 2×10^{-6} mg/l at an absorber vent. This study indicated the total daily emission of hexabromobiphenyl was approximately 0.45 grams. This was equivalent to about 0.07 lb/million pounds. Results of an ambient air/exposure survey in 1974, at the Michigan Chemical Plant, indicated atmospheric levels of Firemaster BP-6 in the bagger area during bagging in the range of 0.01 to 0.03 mg/l air (Kerst, 1976).

1.1.2 Distribution and Consumption History in the U.S.

In recent years the immense loss of life and property to fire has led to demands by both governmental and nongovernmental organizations, for improved fire-resistant materials. Natural fibers have been relatively easy to treat with flame-retardant materials.

Flame retardant materials for synthetics have not been as easily developed. Some brominated organic compounds have been found to be more effective flame-retardants than chlorinated compounds for applications in plastic products.

Polybrominated biphenyls have been some of the more promising flame retardants developed for synthetic materials. These materials have been able to meet flame-resistance performance requirements, and are also economically feasible. Most important, they have little effect upon the flexibility of the base compounds. For these reasons extensive interest has been shown in PBBs as flame retardants, especially hexabromobiphenyl, octabromobiphenyl, and decabromobiphenyl. (EPA, 1975).

The only PBB product to reach large scale commercial production in the U.S. was hexabromobiphenyl which was marketed as Firemaster BP-6 by Michigan Chemical Company. However, several other companies have shown an interest in the use of decabromobiphenyl and octabromobiphenyl, as well as hexabromobiphenyl, as flame retardants.

Prior to the halt in production of hexabromobiphenyl in November, 1974, the chemical had three main commercial uses as a flame retardant:

(1) In ABS plastics
(2) In coatings and lacquers
(3) In polyurethane foam

Information from Michigan Chemical Company contained in an earlier report (EPA, 1975) indicates that BP-6's use as a flame retardant in thermoplastics was confined to those products which do not come into contact with food or feed and which are not used in fabrics subject to human exposure. The types of products in which BP-6 was used and the approximate percentage used in each application are listed in Table 1-2. No commercial uses of the octabromobiphenyl and decabromobiphenyl in the U.S. were reported in the time period 1970-1974. This is probably due to the fact that the hexabrominated compound was less expensive and equally effective.

TABLE 1-2. DOMESTIC USES FOR HEXABROMOBIPHENYL
(EPA, 1975)

Industry	Approximate Allocation of Total Firemaster FB-6 Produced (%)	Examples
Business machines and industrial equipment	48	Typewriter, calculator and microfilm reader housings. Business machine housings.
Electrical	35	Radio and TV parts, thermostats, shaver and hand tool housings.
Fabricated products	12	Projector housings, movie equipment cases.
Transportation	1	Miscellaneous small automotive parts, i.e., electrical wire connectors, switch connectors, speaker grills.
Miscellaneous	4	Small parts for electrical applications, motor housings, components for industrial equipment.

1.1.2.1 Former Consumption Sites and Uses

Since the customer lists of Michigan Chemical Co. are considered confidential and were not disclosed to AAI, the major former consumption sites (i.e., consumption exceeded 20-30,000 pounds per year) are discussed for the three use categories and summarized in Table 1-3.

The chief consumer of PBBs as flame retardants in ABS plastics was Borg-Warner Corporation, where peak consumption may have been of the order of two million pounds in 1974 (EPA, 1975). These plastics were used chiefly for small appliance and automotive applications, and may have had a PBB content of about 10%. The sites at which PBB was used include Parkersburg, W. Va.; Ottawa, Ill. and Oxnard, Ca. However, Borg-Warner states that they no longer use PBB as a flame retardant and have no stocks of the material on hand (Arthur, 1977). They are using other brominated aromatics as substitutes. The flame retardant line of plastics produced by Borg-Warner represents only a small portion of their total production of ABS plastics.

Prior to 1975, Standard T Chemicals used Firemaster BP-6 as a flame retardant in cable coatings. They used an estimated 75,000 pounds of the hexabromobiphenyl per year in their Staten Island, New York plant (EPA, 1975). They no longer use PBBs as flame retardants, nor do they have any in stock (Waterbury, 1977). Since 1975, they have used organophosphates such as tricresyl phosphate, triphenyl phosphate, and cresyl diphenylphosphate as alternative flame retardants. The selection of any given material is based on availability and price vs. performance factors. The company is also looking into the polybrominated biphenyl oxides as possible flame retardants. Again, only a small portion of their total production of coatings are flame retardants.

TABLE I-1. MAJOR FORMER CONSUMPTION SITES

COMPANY & SITE	USE	APPROXIMATE DATE CEASED USE	REASON
Standard T Chemical Staten Island, N.Y.	Fire retardant coatings for industry	1974	Michigan Accident
Borg-Warner Parkersburg, W. Va. Ottawa, Ill. Oxnard, Ca.	Fire retardant in ABS plastics	1974	Michigan Accident
B.A. Burkart Mfg. Co. (Burkart-Randall Div. of Textron Mfg. Co.) St. Louis, Mo. Corry Foam Products Co. (Div. of Firestone) Milan, Te. Corry, Pa.	Fire retardant in polyurethane foam for auto upholstery		Auto manufacturers advised them to cease using PBBs as a F.R. in foam since the ultimate disposal (incineration of automobiles) was not believed to occur at a sufficiently high temperature to combust the PBBs, which would then accumulate in the environment

Hexabromobiphenyl was also used as a flame retardant in polyurethane foam for automobile upholstery. Two of the larger consumers were E.A. Burkart Manufacturing Company (Burkart-Randall Division of Textron Manufacturing Company), in St. Louis, Mo., and Corry Foam Products (Division of Firestone Tire and Rubber Company) at Milan, La., and Corry, Pa.

Burkart reports that they are no longer using FBB as a flame retardant in the foam, but would not disclose their substitute materials as they are considered proprietary (Gilda, 1977). The equipment which had been used for processing the polyurethane foam was dismantled after the Michigan accident.

Corry Foam Products reports that they stopped using FBB as a flame retardant in polyurethane foam in 1973 (Lunderville, 1977). The automobile companies advised them that they did not want their suppliers to use these materials because the ultimate disposal of scrap automobiles by incineration was not believed to take place at a sufficiently high temperature to burn the PBBs. This would lead to the possibility of the compounds accumulating in land fills, where there would be little opportunity for degradation. Corry no longer has any stocks of PBBs on hand.

Dow Chemical Company reported the production of experimental quantities of octabromobiphenyl in the early 1970's. This was tested for use as a flame retardant for polyester fibers by both Dow and DuPont. Based on toxicity data, the testing was discontinued and the process never used commercially (Morris, et al., 1973).

1.1.2.2 General Consumption Process Chemistry for the Main Commercial Uses

The major PBB consumers provided only limited data concerning the process chemistry for their flame retardant products because they consider this information proprietary. For all applications, the process is basically one of physical blending. The PBBs are not functional additives, and upon blending with the dry solid or liquid polymeric material, provide filler-type flame retardant action in addition to the chemical release of HBr if ignited.

The major user of the hexabromobiphenyl (as Firemaster BP-6 from Michigan Chemical) was Borg-Warner Corporation. Their flame-retardant ABS plastics were processed in the same manner as the regular ABS plastics, which is reported to be a dry mixing and extrusion process. The resin and flame retardant components are mixed in a Banbury mixer until the flux point of the ABS resin is reached and the hexabromobiphenyl flakes are melted. The mixture is extruded, pelletized and cooled. Although it was indicated in a previous source (EPA, 1975) that these pellets are water cooled, it is believed that air cooling is the preferred method.

In the production of flame retardant cable coatings, Standard T Chemical was the major consumer of hexabromobiphenyl. Again, the process involved blending procedures.

Neither would former consumers of PBBs for flame retarded polyurethane foam provide details of their fabrication processes, other than to state that standard blending equipment was used (Builds, 1977; Lundervills, 1977). One company (Burkart Manufacturing Company) dismantled the equipment used for processing polyurethane foam and PBB shortly after the Michigan accident. Whether or not non-flame retarded products were processed in the same equipment used to produce PBB-containing compounds was not determined.

1.1.2.3 Potential Use Categories for PBBs

This section discusses potential uses for the PBBs based on a review of the patent and technical literature for the past ten years.

Thirty-four applications of PBBs found in this literature are summarized in Table 1-4. The majority related to the use of the PBB as flame retardants in polymeric materials. Other claims included self-extinguishing properties, improved wearability and machineability; improved luster or color in the case of thermoplastics; and improved luster, dyeability and wearability in the case of textiles.

Six applications of PBBs for other than flame retardant purposes were found, including use in chemical synthesis to prepare biphenyl esters (Knowles, 1972) or in a modified Wurtz-Fittig synthesis (Argus Chem. Co., 1968); their use in light sensitive compositions to act as color activators (Manos, 1970), their use as molecular weight control agents for polybutadiene (Greenlinger, 1969), their use as wood preservatives (Mischulin, 1974), and their use as voltage stabilising agents in electrical insulation (Simplex Wire and Cable Co. 1966, 1967). They are also described as being functional fluids (Brown, 1966) because they exhibit the properties of heat conductors and plasticisers and can also function like a dielectric media. Table 1-5 relates the patent assignments to the assignees, who are also listed in the bibliography.

TABLE 1-4. POTENTIAL USE CATEGORIES FOR POLYMERIZED EPOXIDILS

[illegible]	[illegible] to [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]			Michigan Chem. (1972)	Michigan Chem. (1972)		
[illegible]			Union Carbide (1972)			
[illegible]			DeSoto Chem. (1972)	DeSoto Chem. (1972)	DeSoto Chem. (1972)	
[illegible]						Interez (1972)
[illegible]			General Electric (1972)			
[illegible]			Union Carbide (1972)			
[illegible]						Imperial Chemicals Ltd. (1972)
[illegible]	Monsanto Chemicals Ltd. (1972)					
[illegible]			PPG (1972)			
[illegible]			PPG (1972)			
[illegible]						General Electric (1972)

*Note: Included Epoxy and Resin-modified paint.

TABLE 1-4. POTENTIAL USE CATEGORIES FOR [illegible] MONOMERS (cont'd)

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]					
[illegible]	[illegible]			[illegible]	[illegible]	
[illegible]	[illegible]			[illegible]	[illegible]	
[illegible]			[illegible]			
[illegible]					[illegible]	
[illegible]				[illegible]	[illegible]	
[illegible]						[illegible]
[illegible]				[illegible]	[illegible]	
[illegible]		[illegible]				
[illegible]					[illegible]	
[illegible]				[illegible]	[illegible]	

[illegible]

TABLE I-4. POTENTIAL USE CATEGORIES FOR POLYMERIZED MONOMERS (cont'd)

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]			Union Carbide (1974)	Chevron Chemical Co., U.S. (1974)	Chicago Specialty Co. (1972)	
[illegible]			Union Carbide (1971)			
[illegible]					Dow Chemical (1971)	[illegible] (1971)
[illegible]						[illegible] (1972)
[illegible]	Dow Chemical Co. (1972)		National Starch and Chemical Co. (1972)	*Dow Chemical Co. (1972)	Dow Chemical Co. (1972)	
			Milliken Research Corp. (1972)			
[illegible]	Dow Chemical Co. (1972)			*Dow Chemical Co. (1972)	Dow Chemical Co. (1972)	
					[illegible] (1972)	
[illegible]		General Electric (1972)				
[illegible]		Chemische Werke Hüls A.G., F.R. Germany (1970s and 1980s)				
[illegible]						[illegible] (1972)

*Dow Chemical Company and Dow Corning Corporation

TABLE 1-4. POTENTIAL USE CATEGORIES FOR POLYBROMINATED BIPHENYLS (cont'd)

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]				
		[illegible]				
		[illegible]				
[illegible]			[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]				
[illegible]						[illegible]

[illegible]

TABLE 1-3. PATENT ASSIGNMENTS BY COMPANY

ALLIED CHEMICAL CO.	1975	Koch, P.J. et al.	J. Appl. Polym. Sci. 19(1).
AMERICAN CYANAMID CO.	1972	Murray, R.	U.S. Patent 3,659,077.
ARGUS CHEMICAL CO.	1968		Brit. Patent 1,138,896.
BASF A.-G.	1973	Wurmb, R. et al.	Ger. Offen. 2,236,931.
	1974	Seydl, W.	Ger. Offen. 2,307,283.
	1975	Horm, F. and W. Seydl	Ger. Offen. 2,416,844.
	1976	Schlecking, K. et al.	Ger. Offen. 2,438,102.
BERK LTD.	1971	Abbott, C.J.	Ger. Offen. 2,110,219.
CELANESE CORP.	1973		Brit. Patent 1,340,013.
	1974	Perard, R.	Ger. Offen. 2,335,009.
	1975	Rossaert, R.	Canada Patent 966,259.
CHEMISCHE FABRIEK KALK G.m.b.H	1962	Hahn, H.	Ger. Offen. 1,131,006.
	1964	Lampe, W.	Ger. Offen. 1,169,119.
	1966	Jenkner, H. and H. Muller	Ger. Offen. 1,226,780.
	1966	Jenkner, H.	U.S. Patent 3,283,965.
CIBA-GEIGY A.-G.	1967	Mayer, F. et al.	Ger. Offen. 2,428,390.
CITIES SERVICE CO.	1971	Green, J. and J. Vernaci	U.S. Patent 3,730,942.
DOW CHEMICAL CO.	1972	Mills, J. et al.	Ger. Offen. 2,150,601.
E.I. DU PONT	1970	Manos, P.	U.S. Patent 3,390,995.
	1972	Knowles, R.	U.S. Patent 3,636,082.
FA. UGINE KUHLMAN, PARIS	1970	Hagy, G.	Gen. Offen. 1,950,607.
FIRESTONE RUBBER AND TIRE CO.	1975	Lawson, D. and D. Lohr	U.S. Patent 3,867,327.
FMC	1972	Wright, G. and H. Beacham	Ger. Offen. 2,105,188.
	1973	Beacham, H.	Ger. Offen. 2,246,657.
	1974	Kwapka, W.	Ger. Offen. 2,402,803.
	1974*		Fr. Demande 2,213,491.
	1975	Gresham, J.	Ger. Offen. 2,443,957
GENERAL ELECTRIC CO.	1968	Gowan, A.C.	Fr. Demande 1,512,082.
	1972	Hoof, W.	Ger. Offen. 2,037,510.
	1973	Nicodemus, P. and H. Wilson	U.S. Patent 3,772,455.
	1975	Copper, G. and V. Abolins	Ger. Offen. 2,446,452.
GENERAL TIRE AND RUBBER CO.	1972	Fabris, H. et al.	Ger. Offen. 2,134,113.
GOODYEAR TIRE AND RUBBER CO.	1973	Callander, D.	U.S. Patent 3,909,489.
IMPERIAL CHEMICALS LTD.	1974	Tyler, G. et al.	U.S. Patent 3,839,160.

TABLE I-3. PATENT ASSIGNMENTS BY COMPANY (continued)

M & T	1975	Touvai, I.	U.S. Patent	3,912,792.
MICHIGAN CHEMICAL CO.	1973	Lindemann, R. and J. Anger	Ger. Offen.	2,262,779.
MONSANTO CHEMICALS LTD.	1966	Brown, J.P.	Brit. Patent	1,029,874.
	1973	Parts, L. and J. Miller	U.S. Patent	3,766,177.
	1974	Parts, L. and J. Miller	U.S. Patent	3,825,520.
NATIONAL DISTILLERS AND CHEMICAL CORP.	1969	Crenninger, L. and L. Hanks	U.S. Patent	3,448,093.
PHILLIPS PETROLEUM CO.	1974	Underwood, J. et al.	U.S. Patent	3,850,882.
SEC. OF THE ARMY, U.S. GOV.	1969	Rosso, E.	U.S. Patent	3,431,221.
SIMPLEX WIRE AND CABLE CO.	1966		Brit. Patent	1,021,681.
	1967	Gross, R.E.	U.S. Patent	3,350,312.
UNION CARBIDE CANADA, LTD.	1974	Goeckel, G. and H.Larsen	Ger. Offen.	2,404,537.
	1975	Goeckel, G. and H.Larsen	Ger. Offen.	2,507,289.
	1975A	Goeckel, G. and H.Larsen	U.S. Patent	3,927,141.
UNIVERSAL OIL PRODUCTS, CO.	1973	Cyba, A.	U.S. Patent	3,723,383.
WHITE CHEMICAL CO.	1974	Mischulin, V.	Ger. Offen.	2,352,923.
	1975	Mischulin, V.	U.S. Patent	3,877,974.

Five of these patents are discussed in an earlier report (EPA, 1975), to which the reader is referred for details as to the proposed process technology. These include the use of PBBs and phosphonium bromides as flame retardants for olefin polymers (Murray, 1972), the use of hexabromobiphenyl with other flame retardant components with a variety of base plastic materials (Cyba, 1973), PBBs as part of a mixture yielding non-drip, self-extinguishing polyethylene (Green, 1971), the use of a combination of tetrabromobiphenyl, hexabromobiphenyl and octabromobiphenyl in a flame and moisture resistant material for impregnating fibrous insulating materials for wire and cable (Nicodemus, 1973), and the use of octabromobiphenyl as a flame and smoke retardant in styrene polymers (Parts, 1973). All of the companies to whom the above patents were assigned were contacted, and none indicated that they were using the patent or planned to be using it in the near future (EPA, 1975). Additional contacts with potential users verified that no company with the capability of utilizing the PBBs in any of their products contemplated doing so.[6]

1.1.3 Disposal and Ultimate Fate

PBBs were used chiefly in the formulation of flame retardant plastics. As such the disposal and ultimate fate of PBB would be the same as the plastic component. Information concerning the probable fate of PBB in the environment was reported earlier (EPA, 1975) as follows:

> "Although no data on soil migration of BP-6 are available, a Michigan Chemical spokesman believes that migration is minimal. This opinion is based on two factors: (a) BP-6 is known to be tightly bound into the plastic into which it is incorporated; and (b) a Monsanto study on polychlorinated biphenyl migration in soil indicates that such compounds, especially the highly chlorinated biphenyls, exhibit an extremely small migration tendency. Since BP-6 should exhibit properties similar to the higher polychlorinated biphenyls, BP-6 does not seem to be easily leached from the soil."

[6]Private industrial sources.

Norris et al. (1973), conducted a study on leaching of decabromodiphenyl oxide (DBDO) from pellets of acrylonitrile-butadiene-styrene (ABS) terpolymer containing DBDO. An analysis of aliquots showed that the extraction of DBDO was below limits of detection for bromine (0.5 ppm) in many of the samples. The lack of increase of bromine concentrations with time and the erratic values of bromine determined are best explained by assuming that extraction of DBPO was previously due to erosion of surface particles. Evidently, migration of DBPO within the plastic was not significant.

A static leaching experiment reported by the same authors in the same article showed no detectable amounts of DBPO in the water (detection limit = 0.075 ppm). Although this study was not done with PBBs, similar results for PBB can be postulated based on the similarity in properties of the two chemicals.

The ultimate fate of wastes resulting from PBB manufacture is reported by Michigan Chemical to be in a landfill operation.

A report by Hesse (1977) stated that analyses of water and sediment samples obtained in the vicinity of the Gratiot County landfill on March 1, 1977 showed PBB concentrations of 0.1 to 0.2 ppb in the water samples and between 0.35 and 1.3 ppm in sediment samples from drainage ditches and a catch basin. The Gratiot County landfill was the disposal site used by Michigan Chemical.

A study by Jacobs and Filanow (1976a) indicated that PBBs were absorbed on soils and that:

(1) absorbtion increased with increasing organic carbon content of soil.
(2) less than 0.6% of the PBB was lost from the soils using leachate quantities 20 times the average Michigan rainfall.

They concluded that PBB present in farm soils should not leach below the depth of incorporation.

It was also demonstrated that orchard grass and carrots grown in PBB contaminated soil "showed no or only very minor uptake of PBB."

These studies corroborate the conclusions reached in the EPA (1975) report quoted above, that "FB-6 does not seem to be easily leached from the soil."

The incineration of plastics containing PBB has been investigated by Benbow and Cullis, (1975). It was found that incineration of plastics containing PBB resulted in the complete conversion of PBB into HBr, CO_2 and H_2O. However, if the plastic material was heated without combustion, then PBB was volatilised without change.

Studies on the ultimate fate of PBB discharged into streams showed that there was a tendency for fish to concentrate the PBB in the fat tissues (Hesse, 1974).

As a result of the accidental contamination of feed that occurred in Michigan, a number of studies showed PBB concentration in liver and fat tissues (EPA, 1975). Milk from affected cows was found to be contaminated with PBB residues as high as 100 ppm.

1.1.4 Market Factors

The market factors affecting the consumption of PBBs were limited to competitive cost-performance characteristics of PBB compared to other flame retardants. With increasing governmental regulations with respect to improving flame retardant properties of plastic and textile materials, the market for such compounds appeared to be growing rapidly.

The subject of toxicity and potential hazard to health and the environment has resulted in an evaluation of chemicals with good flame retardant properties. Risk-benefit studies of these compounds have not been fully documented. Until they are, the general market for flame retardant chemicals must consider the health and environmental hazard in the manufacture, sale, and distribution of this class of chemicals.

Shipping practices for hexabromobiphenyl included shipment by motor carrier or railroad.

The materials were shipped in fiber drums and 5-ply construction bags. (Kerst, 1976).

Spokesman for current manufacturers of octa-and decabromobiphenyl generally confirmed the shipping practices of Michigan Chemical. They reported that their material was shipped from their plant to the docks only in motorcarrier for export via ocean freighter.

When Michigan Chemical Co. produced PBB, they packaged the material in distinctive colored bags. Bags of the same type, but different color were used for magnesium oxide, an animal feed supplement. Despite the fact that the PBB bags were correctly marked, a warehouseman accidentially mixed some pallets containing bags of PBB in the storage area for magnesium oxide. This error resulted in the shipment of some PBB to the Michigan Farm Bureau, who did not read the bag labels, compounding the initial error by mixing the PBB into the animal feed.

Stockpiling of PBB by the manufacturer was done only to the extent necessary to maintain supplies for normal distribution demands.

The consumers also stockpiled PBB, but only to the extent that was normal for their operations. The historical supply-demand position in the United States was in balance. Supply was able to keep up with demand.

There is currently no U.S. domestic sale of PBBs. There would appear to be a growing European demand for decabromobiphenyl as evidenced by increasing exports of this chemical during the past several years (see Section IV).

1.2 SUMMARY OF MANUFACTURING PROCESSES AND END PRODUCTS

Manufacturing processes are considered proprietary by the several companies who make, or have made, polybrominated biphenyls. The patent literature contains a number of references for the processes of the bromination of biphenyls. These patents generally describe the chemical reaction process and refer briefly to recovery, purification and by-products. In most cases, the biphenyl is reacted with bromine and chlorine in a solvent with an aluminum chloride catalyst. These patents, summarized in the following section, are described in an earlier report (EPA, 1975).

1.2.1 Patented Manufacturing Processes

The Dow Chemical Company was issued a patent in 1974 concerning, among other reactions, bromination of biphenyl with bromine chloride under pressure to produce a product containing five bromine atoms on each aromatic ring (Moore et al. 1974). This process consists essentially of brominating biphenyl with bromine chloride (BrCl) in the presence of iron or a Friedel-Crafts catalyst in a closed vessel at or near autogenous pressure to obtain rapid polybromination of the aromatic nucleus. The reaction may suitably be conducted at about room temperature, and is completed in a few hours, with yields in excess of 80% generally being obtained.

Bromine chloride is prepared by mixing equal molar amounts of bromine and chlorine in a closed container; the bromine chloride thus formed is withdrawn from the liquid phase in the vessel.

Decabromobiphenyl, and lower polybrominated biphenyls are prepared by adding a catalyst (aluminum chloride) and biphenyl to a batch reactor, and then slowly adding bromine chloride in 0 to 20% stoichiometric excess. For example, 10 moles of bromine chloride may be reacted with each mole of biphenyl.

As the bromine chloride reacts with biphenyl, the hydrogen chloride formed as by-product is retained in the reactor under essentially autogenous pressure. The pressure may range from 10 to 200 psig during the course of the reaction. The reaction temperature is not

critical; the temperature may range from 10 to 150°C. A solvent, such as methylene chloride, may be used in the reaction, although good conversions and yields are obtained by using excess bromine chloride as the solvent. Best results are obtained when the reactor is operated under essentially anhydrous conditions; water apparently deactivates the catalyst. Essentially complete bromination is generally obtained within a few hours. After the reaction, the solid products are separated from the methylene chloride solvent. The advantages claimed for this process include high product yields, low yields of chlorinated compounds, short reaction periods, and efficient utilization of bromine.

Chemische Fabrik Kalk G.m.b.H., Cologne-Kalk, Germany, obtained both a U.S. and German patent in 1966 for a process of bromination of aromatic compounds, especially diphenyl, diphenyl ether, and mixtures thereof (Jenkner, 1966). The bromination process is carried out at 20 to 65°, using 1.01 to 1.2 g-atoms of bromine chlorine which, at most, is equimolar with respect to the bromine. The product contains at least 4 g-atoms of bromine per mole of aromatic compound used as a raw material. Following completion of the bromination reaction, a quantity of an alkylene (e.g., ethylene or propylene) is added to the reaction mixture to react with the excess bromine with the formation of the corresponding alkylene bromide (dibromoethane). A modification of the process involves the use of alkylene bromide as a solvent.

An example of the application of this process for preparation of brominated diphenyl is described in this patent. Diphenyl (308 parts by weight) was dissolved in 800 parts of ethylene bromide and 4 parts of iron powder were added. Then, 1,430 parts of bromine and 631 parts of chlorine were introduced into the mixture with vigorous stirring over a period of about 3 hr. During the addition of bromine and chlorine, the temperature of the reaction mixture ranged from 20 to 60°C. After the bromination had been completed, the excess bromine contained in the reaction mixture was eliminated by adding ethylene to form ethylene bromide. The pasty reaction mixture was filtered, and the ethylene dibromide obtained as filtrate was suitable for reuse as solvent. The filter cake was washed with ethanol and dried. The dried

solid product contained 1,740 parts of octabromodiphenyl containing 80.9% of bromine and 1.5% of chlorine. This product yield was 93.5% of the theoretical yield.

An improved method for preparing polybrominated biphenyls was described in a patent issued to Ethyl Corporation (Mitchell, 1973). This process consists of reacting an aromatic compound with bromine in the presence of a halogenation catalyst (aluminum chloride or aluminum bromide) and a solvent (methylene bromide) at a temperature sufficient to sustain a rapid reaction rate. Reaction temperatures are below 100°C, and reaction time is from 2 to 10 hours. By-product hydrogen bromide is produced.

When the desired degree of bromination is achieved, the reaction is stopped by quenching with water. According to the patent, the reaction mass is successively washed with acid, alkali, and finally water. The organic layer is then dried by adding sodium sulfate, and the solvent is stripped to recover a crude product. This product can be recrystallized from solvent or washed with solvent followed by solvent stripping in an evaporator. The hydrogen bromide gas is removed from vent gases by scrubbing with sodium hydroxide. Examples of quantities of reactants, operating conditions, and results claimed are summarized in Table 1-6.

From a perusal of permit applications made to the State of New Jersey (1973, 1975, 1976(a), 1976 (b), 1977) it would appear that the process described is generally being followed by the companies who currently manufacture the polybrominated biphenyls. The solvents used differ from the one noted in the patent, and chlorine is introduced to aid the reaction. Separation of the product is by centrifugation. There is no analytic data available to indicate whether or not the introduction of chlorine results in the formation of PCBs as a by-product.

The solvent extract is stripped to recover the solvent, or may be recycled to the next batch. The centrifuged product is dried, and pulverized. An alternative is to dry the product, then melt and flake the PBB on a chilled roll.

TABLE I-6. [illegible]
([illegible] et al., 1974)

Example No.	Reactants (Parts by Weight)				Br_2 Equivalents[a]	Conditions		Products			
						Time (hr)	Temp. (°C)	Weight (parts)	Avg. Br_2 Number[b]	Weight Percent Br	Percent Yield Based on Avg. Br Number
1	17.8	122	157	0.88 $AlBr_3$	9.2	7.2	25-85	97.7	8.69	81.8	Quantitative
2	17.8	122	157	0.99 $AlBr_3$	9.2	4.3	25-98.5	98.2	8.75	84.3	Quantitative
3	17.8	157	200	1.32 $AlCl_3$	8.5	2.5	25-95	85.3	8.4	80.0	92.6
4	17.8	162	200	0.68 $AlCl_3$	8.75	3.0	25-95	95.0	8.41	79.6	Quantitative
5	17.8	169	254	0.38 $AlCl_3$	9.2	2.75	25-95	96.5	8.53	79.6	Quantitative
6	17.8	184	267.5	1.93 $AlCl_3$	10.0	4.0	25-95	95.5	8.85	81.6	97.6
7	17.8	175	250	0.99 $AlCl_3$	9.5	2.1	25-95	100.0	8.9	82.7	Quantitative

[a] Br_2 equivalents are moles of Br atoms available for reaction with biphenyl from Br_2 charged; calculated by dividing moles of Br_2 by moles of $[C_6H_3Cl_2]_2$.

[b] Average bromine number determined by VPC; certain peaks assumed to be tri-, tetra-, penta-, and decabromobiphenyl based on retention time. Area percent used for calculations.

1.2.2 By-Products and End Products

Unreacted bromine may be recovered from the reaction vent gases by scrubbing with the solvent. By-product hydrogen bromide is recovered by scrubbing with water or sodium hydroxide. Bromine may be recovered by treating the sodium bromide solution with chlorine and stripping with steam.

Lower polybrominated biphenyls (hexabromo- and lower) may be carried out from the reactor with the vent gases. If they are not absorbed in the bromine solvent scrubber, they may be carried over to the hydrogen bromide scrubber where they could contaminate the recovered sodium bromide solution and regenerated bromine.

1.2.3 Imports and Exports

There are currently no imports of PBB into the U.S. in commercial quantities. Exports of PBB from the U.S. to Europe, consisting chiefly of the decabromobiphenyl, totalled 805,000 pounds in 1976.

SECTION II. CURRENT MATERIAL BALANCE

2.1 NATURAL SOURCES

There are no data that show any source of any polybrominated biphenyl occurring in the environment naturally.

2.2 MANUFACTURING

There are only two polybrominated biphenyls currently being produced commercially in the U.S. Octabromobiphenyl production in 1976 was reported to be 30,000 lbs. Decabromobiphenyl production in 1976 was reported to be 775,000 lbs.

Air losses as particulate matter at the manufacturing sites, calculated per million pounds produced, amounted to a probable maximum of 900 lbs. in 1976.

There are no data available on liquid losses at the two plants that produced PBBs in the U.S. in 1976. Calculations can be made using batch composition data provided in the Permit Applications to the New Jersey State Department of Environmental Protection (1973, 1976), combined with the reported solubility of PBBs

in water of 20 to 30 ppb. The raw material data contained in the N.J. Permit application shows that 0.23 lbs. of process water is used per pound of product. Making the assumption that this number is valid for all current PBB production methods, then about 185 thousand pounds of water were wasted in 1976. At a 20 ppb solubility, the amount of of PBB lost in liquid wastes in 1976 can be calculated to be 0.0037 lbs.

Accidental production of PBBs in other commercial chemical processes has not been documented. Based on discussions with producers of other chemicals which are intermediates in bromination processes, we have concluded that it would be a small amount, on the order of 500 pounds per year (see Section 5.5).

2.3 IMPORTERS

According to communications from the U.S. Embassies in London and in Germany, there is no exportation of any polybrominated biphenyl to the United States (Cox, 1977, Dept. of State, 1977). A spokesman for Bolchem Corporation, an Israeli bromine producer, stated they do not manufacture any polybrominated biphenyl (Zafran, 1977).

From all available information, there are no other countries in which there are manufacturers of PBB (see Table A-1).

It may be concluded that PBB is not imported into the U.S., except, perhaps, in finished products.

2.4 CONSUMPTION AND USERS

All PBBs currently produced in the U.S. are exported. This has been verified by spokesmen for the two companies which produced commercial quantities of octa- and decabromobiphenyl in the U.S.

2.5 EXPORTERS

According to spokesmen for the two companies manufacturing octa- and decabromobiphenyl in the U.S., the total amount produced was exported. In 1976 this amounted to approximately:

octabromobiphenyl	30,000 lbs.
decabromobiphenyl	775,000 lbs.
Total PBB	805,000 lbs.

2.6 FINAL DISPOSAL AND ENVIRONMENTAL FATE

At present, none of the octa- and decabromobiphenyl produced in the U.S. have been consumed in the U.S. Final disposal of these materials will be made in Europe. It is possible that PBB-containing plastics are used by foreign producers to manufacture various finished products, such as television sets, for export to the U.S. These items would then have their final disposal in the U.S. There is presently no information regarding this matter.

Table 1-1 shows that during the period 1970-1976 approximately 11.8 million pounds of a commercial hexabrominated biphenyl were produced and sold in the United States. Substantially all of this quantity was used in the production of flame retardant plastic products. Based on an estimated 5 to 10 year life of the plastic products, most of the PBB produced in the United States is presently contained in useful products. Within the next five years, these PBB-containing products, such as TV cabinets and business machine housings, will be disposed of through landfills or incineration, and enter the environment.

Based on a PBB content of 10% in ABS resins, it can be estimated that approximately 118 million pounds of plastic products were made flame retardant with PBB. During the period when PBBs were used as a flame retardant (1971-1975) the total production of ABS resins is estimated to be 2.4 billion pounds. About 5% of this estimated production could have been formulated with hexabromobiphenyl (Firemaster FB-6).

2.7 AREA MASS BALANCE

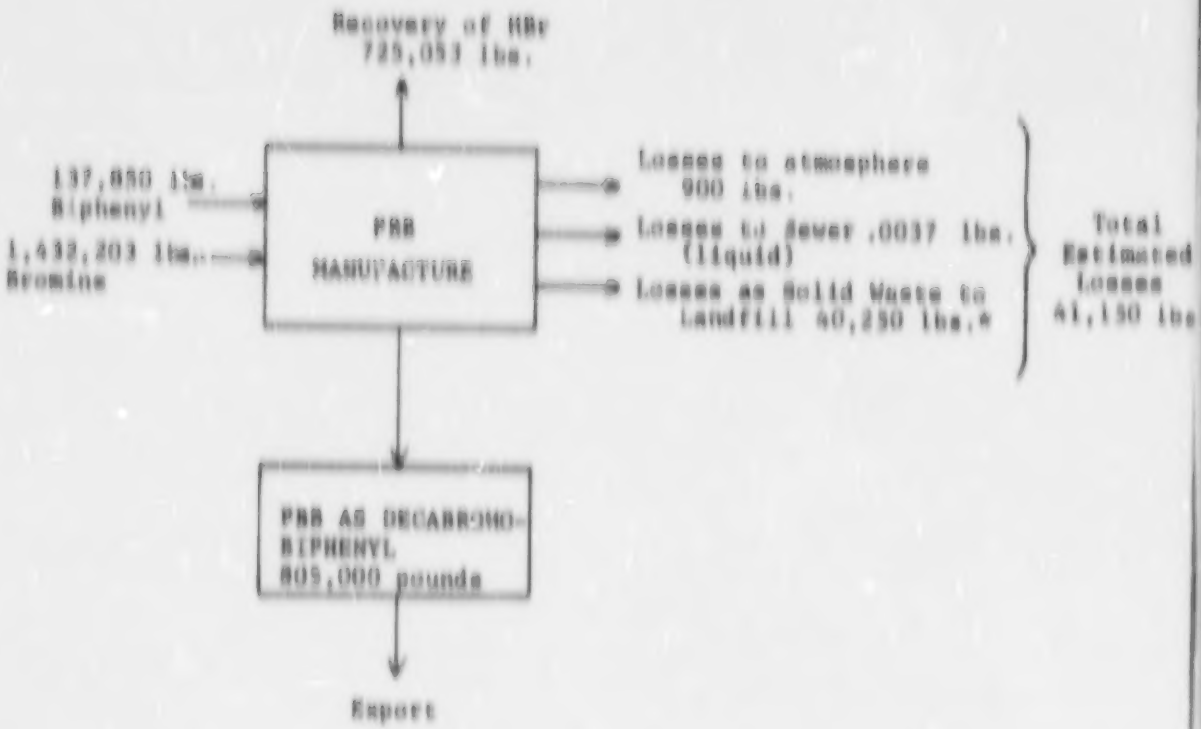
Both companies who manufactured PBB in the U.S. in 1976 are located in New Jersey. Environmental losses of PBB due to manufacturing will be limited to this state at present.

There is no information available to determine if there is any accidental PBB contamination of other brominated products produced by these two companies.

Figure 2-1 shows an estimated input/output summary for current (1976) PBB production, as the decabromobiphenyl. Calculations were based on the stoichiometric equation:

$$C_{12}H_{10} + 10Br_2 \longrightarrow C_{12}Br_{10} + 10\,HBr$$

No data on solid losses at the current production sites are available. Thus, the number given is an estimate based on disposal of hexabromobiphenyl at the Michigan Chemical Co. site (Kerst, 1976). It should be noted, however, that there is no evidence that indicates this loss is paralleled in processes used by the current producers of octa- and decabromobiphenyl.



*See text for estimate description. Probably includes waste catalyst, in addition to PBBs of varying degrees of bromination (exact composition not known).

Figure 2-1. Estimated Input/Output, U.S. Manufacture of PBB as Decabromobiphenyl Equivalent for 1976

SECTION III. MANUFACTURING PROCESSES STUDY

3.1 PURPOSEFUL MANUFACTURING

Octabromobiphenyl and decabromobiphenyl are being produced in the U.S. for export. An estimated 30,000 pounds of octabromobiphenyl and 775,000 pounds of decabromobiphenyl were produced in 1976. There are no current manufacturers of the hexabromobiphenyl.

3.1.1 Manufacturing Sites

The earlier survey (EPA, 1975) cited two companies, Michigan Chemical Co. and White Chemical Corporation, as being the only domestic producers of polybrominated biphenyls during the past decade. However, a third company, Fine Organics Division of Hexel Corp. has produced commercial quantities of the decabromobiphenyl since 1973. In view of the current investigations concerning the polybrominated biphenyls this company has suspended all production of this chemical.*

Table 3-1 summarizes current commercial domestic production levels and estimated total capacity. Capacity estimates have been derived from data supplied by the New Jersey Department of Environ-

*Personal communication with private industry sources.

TABLE J-1. COMMERCIAL DOMESTIC PRODUCTION AND ESTIMATED PRODUCTION CAPABILITIES FOR POLYBROMINATED BIPHENYLS, 1976

(Industry Sources, 1977, New Jersey Dept. of Environmental Protection, 1977)

CONTINUED, 1ST TIER

Hexabromobiphenyl	Octabromobiphenyl	Decabromobiphenyl	Maximized Capacity
0	20-30,000	775,000	5,725,000

mental Protection (1977). The equipment can be used for other bromination processes, as demand warrants. It should be noted that all PBBs produced by these companies are for export, principally to Europe. None are sold domestically, and no hexabromobiphenyls are currently being produced in the U.S.

In addition to the current commercial producers, there are four chemical companies who manufacture the lesser brominated biphenyls, chiefly the mono- and dibromo-compounds, e.g. 4-4'-dibromobiphenyl. These are produced in small batches varying from 100 gm to one kg, on a custom order basis for laboratory use. Table 3-3 lists the suppliers of the lower brominated biphenyls. It should be noted that Eastern Chemical (Globus, 1977) states they do not produce 4-bromobiphenyl, but maintain a "small" inventory of this and other unspecified PBBs. They did not indicate the source of their supply.

Both Ethyl Corporation (Baton Rouge, La.) and Fairfield Chemical Company (Blythewood, S.C.) were previously reported to be small-volume producers of brominated biphenyls (EPA, 1975). Ethyl Corporation currently reported that to the best of their knowledge, they have not produced any quantities of any brominated biphenyls within the past five to six years (Buchholz, 1977). Fairfield Chemical Company stated that they had at one time acted as a wholesaler for brominated biphenyls manufactured in England by Specialty Organics. These had consisted chiefly of 2-bromobiphenyl and 4-bromobiphenyl, handled in approximately 100 gm lots. However, they do not have any brominated biphenyls on inventory at the present time (Allen, 1977).

Chemical Samples Company (Columbus, Ohio) reported that they had produced 4-4'-dibromobiphenyl several years ago, but no longer produce it. No more than a few kilograms were produced and sold. Production ceased because it was uneconomical (Greelee, 1977).

3.1.2 Manufacturing Processes by Site

Polybrominated biphenyls may be defined by the following general chemical formula:

TABLE 3-2. DOMESTIC PRODUCERS OR SUPPLIERS OF LABORATORY QUANTITIES OF BROMINATED BIPHENYLS, 1976

(Industry Sources, 1977*)

COMPANY	COMPOUNDS	APPROXIMATE QUANTITIES PRODUCED
Biochemical Laboratories, Inc. Hawthorne, CA.	All degrees of bromination on request	100 gm batches
Chemical Samples Co.** Columbus, OH.	4-4'-dibromobiphenyl	1 kg batches
Columbia Organic Chemical Co. Columbia, S.C.	mono- and dibromobiphenyls	1 kg batches
Eastern Chemical Hauppage, N.Y.	inventories of various degrees of bromination	-
Research Organic/Inorganic Chemical Corp. Bellsville, N.J.	4-4'-dibromobiphenyl, other degrees of bromination	1 kg batches
K & K Laboratories Plainview, N.Y.	2-bromobiphenyl 3-bromobiphenyl 4-bromobiphenyl	1 gm to 1 kg batches

*Industry Sources: Berg, 1977; Gergel, 1977; Greenlee, 1977; Globus, 1977; Brill, 1977; Weiss 1977.

**No production since 1975.

where the subscripts (n & m) represent the bromine content of the compound. Bromination of biphenyls occurs in stages.

Table 3-3 gives physical data for biphenyl, hexabromobiphenyl, octabromobiphenyl and decabromobiphenyl. These data show that the higher the degree of bromination, the lower the vapor pressure, and the higher the melting point and the "boiling" point.

Both White Chemical Corporation (Bayonne, N.J.) and Hexel Corporation, Fine Organics Division (Sayreville, N.J.) manufacture polybrominated biphenyls using essentially the same process. Biphenyl is reacted with bromine in the presence of chlorine, in an organic solvent such as tetrachloroethane or ethylene dichloride, using aluminum chloride as a catalyst. In this Friedel-Crafts type reaction, a measured quantity of solvent is precharged into the bromine absorber hold tank. A measured quantity of water is precharged to the hydrogen bromide solution hold tank. Recirculation is started in both loops. Solvent, chlorine, and biphenyl are blown into the reactor, the catalyst is added, and bromine is pumped in or fed by gravity from a scale tank. The reaction is initiated by heating the batch to 60°C, at approximately atmospheric pressure. Excess bromine is distilled off the product, which has a high melting point (see Table 3-3), and recovered. The bromine is recovered from the solvent and returned for use in the reaction. Hydrogen bromide gas emitted from the reactor is cooled in a heat exchanger and then absorbed by water in the HBr absorber towers. The absorbers and recirculation tanks are vented through an absorber which exhausts into a packed unit water scrubber.

After the desired degree of bromination has been attained, the reaction mass is quenched with water. This releases additional quantities of hydrogen bromide, to the vent scrubbers. The aqueous layer, containing the catalyst, is separated and sent to waste disposal. The PBBs suspended in the solvent are removed by centrifugation, solvent washed, tray dried, then ground to a powder. White sent the centrifuge cake to Fluidized Processing for drying and grinding (EPA, Region II, 1977).

The process is carried out in glass-lined steel reactors. Table 3-4 is a summary of the manufacturing process.

TABLE 3-1. PHYSICAL DATA FOR BIPHENYL AND BROMINATED BIPHENYLS

(Norris et al., 1973; EPA, 1975)

	Biphenyl	Hexa-* Bromo-Biphenyl	Octa-** Bromo-Biphenyl	Deca-* Bromo-Biphenyl
Melting Point	70°C	72°C	200-250°C	380-386°C
Boiling Point	255.6°C	-		
Vapor Pressure (mmHg)				
90°C		.000076		
140°C		0.0076 mm		
220°C		0.76 mm		
Volatility % Wt Loss				
≤1			250°C	
≤5				341°C
≤10			310°C	363
≤25				388
≤50			350°C	
Solubility g/100g Solvent				
Acetone		6	1.8	
Benzene		75	8.1	
Solubility in H_2O, ppb		11	20-30	

*EPA, 1975

**Norris et al., 1973

TABLE 3-4. SUMMARY OF THE MANUFACTURING PROCESS FOR PBBs

Raw Materials	Intermediates	By-Products	Product Grade or Type	Capital Value	Process	Distribution
Benzene Aluminum Chloride Tetrachloromethane or Ethylene Dichloride Biphenyl Chlorine	none	HBr	Commercial	< $500,000	Friedel-Crafts type reaction	Export

3.1.3 Transportation and Handling

The polybrominated biphenyls are shipped and handled as dry powders. None of the chemicals in this class are listed in the Department of Transport List of Hazardous Materials, and no special handling methods have been developed for transport, storage or disposal of spills. The compounds are packed in 50 pound bags or 100 pound fiber drums for shipment. The major exporter of polybrominated biphenyls reports that the material is shipped to Europe via water carrier.

3.1.4 Current Environmental Management Practices

This section discusses the available data concerning losses to the environment and pollution control practices for the two current (as of Dec. 1976) manufacturing sites, White Chemical Company (Bayonne, N.J.) and Fine Organic Division of Hexel Corporation (Sayreville, N.J.). A study on the environmental management at the former PBB manufacturing site at Michigan Chemical Co. (St. Louis, Michigan) which is of historical interest, was discussed in Section 1.1.

3.1.4.1 Losses or Disposal via Air, Water and Solids

Losses of PBBs to the environment at manufacturing sites occur through:

(1) Emission to the air from the vents of the hydrogen bromide recovery system

(2) Losses in waste waters resulting from the quenching and washing of the PBBs as they are recovered from the reaction mass

(3) Solid losses to landfills resulting from drying, handling of the product, shipping and transportation.

Air emissions have been calculated by one manufacturer for the following charge (New Jersey State Dept. of Environmental Protection, 1973):

Raw Material	Quantity, lbs/batch
Bromine	3700
Aluminum Chloride	50
Biphenyl	460
Chlorine	1060
Ethylene Dichloride	4000
Total	9270

The calculated air emissions from this operation based on three 8-hour batches per day, are shown in Table 3-5. The data represent emissions resulting from the use of control apparatus as discussed in Section 3.1.4.3.

TABLE 3-5. TYPICAL AIR EMISSIONS DURING PBB MANUFACTURE
(New Jersey State Dept. of Environmental Protection, 1973)

Air Contaminant	Quantity, lb./hr.
Hydrogen Chloride	0.017
Bromine	0.009
Ethylene Dichloride	0.339
Total	0.355

A second manufacturer reported similar air emissions, i.e., total quantity of contaminants less than 0.5 lbs./hr., for a comparable process (New Jersey State Dept. of Environmental Protection, 1976).

The two sites for which air emissions data are reported are both concerned only with the production of the higher brominated biphenyls, i.e. octabromobiphenyl and decabromobiphenyl. The probability of emitting the higher PBBs from hydrogen bromide recovery system vents should be extremely low. For example, the vapor pressure of the hexabromobiphenyl at 90°C has been reported to be 7.6 x 10-1 mm Hg (EPA, 1975). On the basis of partial pressure, this would be equal to 100 ppb if air were passed over the pure chemical. The vapor pressure of the octa- and decabromobiphenyl is substantially lower, hence the air emission of these chemicals would be proportionally less.

Losses of PBBs in waste waters can occur by solution or as a suspension from washing of the product, or washing equipment and floors.

During the bromination process, water is used to quench the reaction mass once the desired degree of bromination is achieved. This aqueous layer, containing the catalyst and parts per billion of the PBBs, is separated and sent to the chemical sewer. Since the solubility of the higher PBBs in water is very low, on the order of 10 to 20 ppb, the probability of entry of PBBs into the environment from this source is very low, except for particulate suspension.

Both manufacturers have reported the use of centrifugation equipment for removal of solids from the reaction products. Losses in the form of a suspension of PBBs in plant wash water would be dependent on general plant housekeeping and the efficiency of settling equipment prior to out flow into the local waste water system.

Solids emitted from drying, grinding and packaging equipment in the form of dusts, can be recovered using dust control equipment, to effect substantially complete solids removal (99+ percent). However, no data on solids losses has been reported. Any solids that might result from manufacturing operations can be disposed of in sanitary landfills.

3.1.4.2 Reclamation

In the manufacture of polybrominated biphenyls, the excess bromine, the reaction solvent, and by-product HBr are recovered.

The vaporized solvent, which may be styrlene dichloride or tetrachloroethane, and the unreacted bromine are recovered by a combination of condensation and absorbtion. These materials are recycled to the next batch.

The solvent in the reaction mass is separated from the polybromonated biphenyl by centrifugation or filtration. It may be recycled to the next batch, or it may be recovered in a pure form by distillation.

Hydrogen bromide, a by-product of the bromine-biphenyl reaction, is recovered by scrubbing with water. The process is described in Section 3.1.4.3 below.

3.1.4.3 Pollution Control Practices and Technologies

Typical pollution control practices for the recovery of the hydrogen bromide (HBr) generated during the reaction, excess bromine (Br_2) and solvent are shown in Figure 3-1. These materials, emitted during the reaction, are cooled in a condenser or heat exchanger; the solvent and Br_2 removed in the Br_2 scrubber and sent to the Br_2-solvent solution hold tank for reuse. The HBr gas is absorbed using sodium

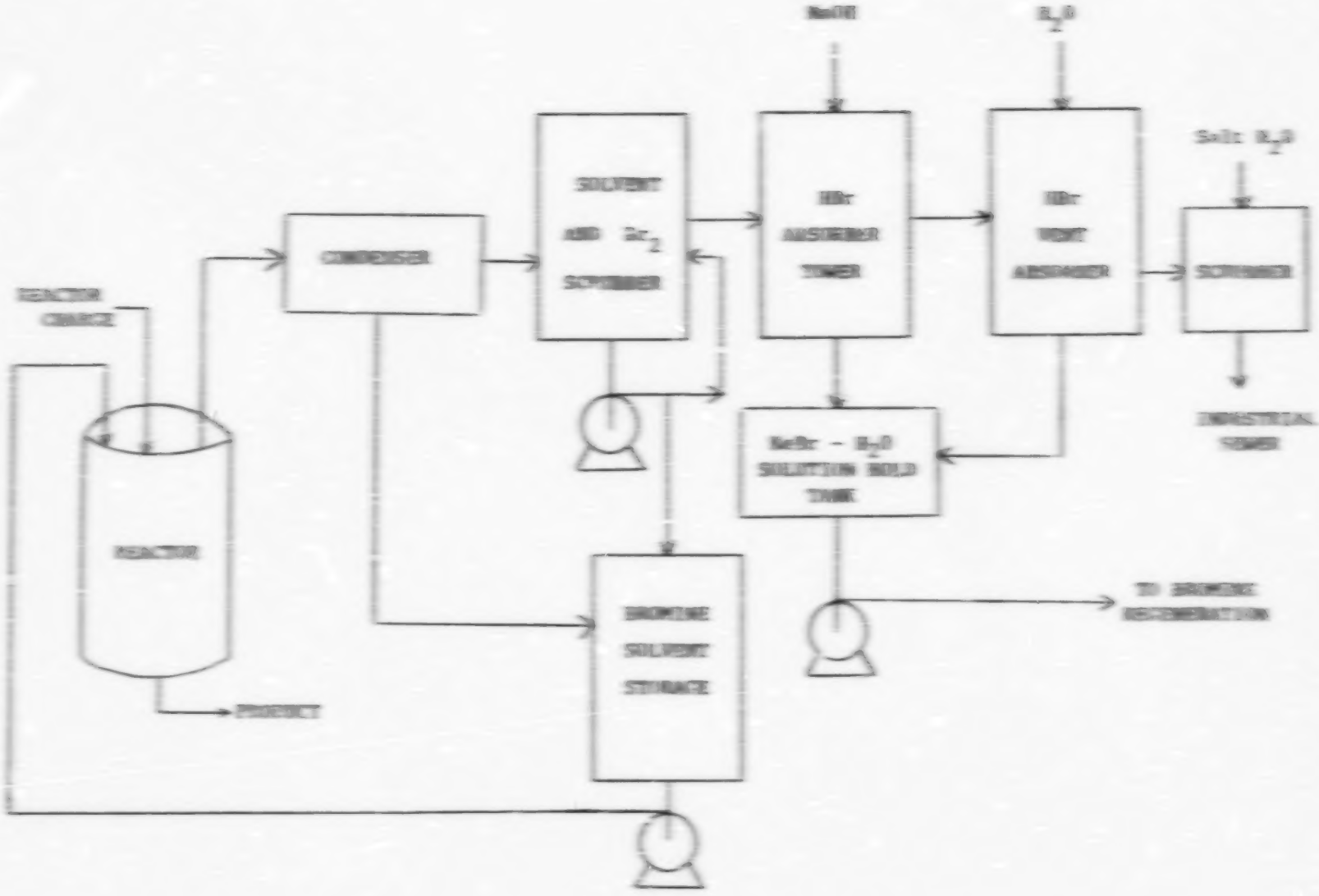


Figure 3-1. Flow Diagram for Typical Recovery of Hydrogen Bromide, Bromine and Solvent

hydroxide solution in an absorbtion tower. These typically consist of glass columns packed with ceramic saddles; the recovered HBr (as sodium bromide) is sent to a bromine regeneration unit.

Absorbers and recirculation tanks are vented through an absorber which exhausts into a salt water scrubber. When bromination is completed and quench water added, the gases emitted, chiefly HBr, are absorbed as above. All outlet water goes to an industrial sewer.

Pollution control technologies are also applied to the grinding and collection of the polybrominated biphenyl products. Typically, the apparatus is a bag type dust collector with exhaust fan that draws product laden air through filter bags. Since the air contaminant is a saleable product it is further processed and recovered.

3.2 CHEMICALS PRODUCED WITH PBB AS AN ACCIDENTAL IMPURITY BY-PRODUCT

Other chemicals produced with the polybrominated biphenyls as accidental impurities can occur either in the final product or in the waste stream from the manufacture of PBBs.

3.2.1 Accidental Impurities in the PBB Product

The major source of impurity that occurs in PBBs results from the spread in the degree of bromination. Most of the commercially available polybrominated biphenyls, and those which have been tested extensively, are mixtures of various brominated biphenyls and generally contain amounts of hexa-, hepta-, and octabrominated biphenyl. For example, the composition of Firemaster BP-6, marketed as a hexabrominated biphenyl was given as follows:

Hexabromobiphenyl	63%
Heptabromobiphenyl	14%
Pentabromobiphenyl	10%
Tetrabromobiphenyl	2%
Other brombiphenyls	11%

More than one-quarter, and possibly one-third, of the product consisted of lower brominated biphenyls which are more volatile. It is the lower brominated materials that are most likely to occur as a PBB impurity

due to incomplete bromination reaction.

The major current domestic producer of PBBs, who exported about 750,000 pounds of decabromobiphenyl in 1976, reports that their material is more than 98 percent pure, the remaining 2 percent being nonabromobiphenyls. It is manufactured by a proprietary process in a chlorinated solvent which completely brominates the biphenyl and results in no brominated by-products.

Other accidental impurities which can be produced with the PBBs result from impurities in the biphenyl feed material. Two major manufacturers were contacted concerning the possibilities of impurities in the biphenyl grade used for bromination. One reported* their biphenyl contained less than 5 ppm total impurities; no analysis was available. The other manufacturer reported* that there were typically less than 0.5% impurities in their bromination grade biphenyl. These had been identified as:

Toluene
Naphthalene
Methylene biphenyl (fluorene)
Various methyl biphenyls

No data were available detailing whether these chemicals would undergo bromination under the conditions of the biphenyl bromination reaction.

* Private industry source.

3.2.2 Accidental By-Product Impurities in Waste Streams from PBB Manufacture

There are no data available on actual impurity by-products in the waste stream formed along with the manufacture of PBBs. It is known that HBr formed as a reaction by-product is reclaimed. Other accidental impurities which could be produced with the PBBs and appear in the waste stream could be the result of impurities in the biphenyl. Any contaminants which might result from biphenyl impurities would probably be concentrated in the tar stream. The solvent in which the reaction is carried out is reused and may eventually concentrate any brominated impurities. A waste stream pollution problem can occur if the tar stream is disposed of in landfill instead of by proper incineration.

SECTION IV. CONSUMPTION PATTERNS

There are currently no domestic commercial consumers of any polybrominated biphenyls. All consumer industries have found alternative flame retardant additives to replace the hexabromobiphenyl in their plastics formulations.

4.1 IMPORTERS

In discussions with American and European producers, former producers, and former consumers of the PBBs, AAI has been unable to uncover any indications of imports of any polybrominated biphenyls within the past year. Since all industry reports confirm that there are no domestic consumers of PBBs, it seems unlikely that an import market exists.

F.W. Berk Co., England, reported that they formerly produced the decabromobiphenyl, Flamex B-10. They no longer produce it or any other PBBs. They do not believe there are any other current PBB producers in Britain (Cox, 1977).

AAI received unconfirmed reports from several industry sources, here and abroad, that an Israeli company was producing PBBs in Holland. This company has been identified as the Suichem Dead Sea Bromine Group of Suichem, Inc.; with two bromine plants in Holland. Suichem reported that they have not made, and do not plan to make, any of the polybrominated biphenyls. However, they say they may produce polybrominated biphenyl oxides in the future (Safran, 1977).

According to industrial sources, Kalk A.G., Cologne-Kalk, Germany, is reported to be producing both the hexabromobiphenyl and the octabromobiphenyl. It has been confirmed that they are not exporting PBBs to the U.S. (Department of State, 1977).

The information on potential sources of imports of PBBs into the U.S. is summarized in Table 4-1.

4.2 EXPORTERS

Decabromobiphenyl, and small quantities of octabromobiphenyl (no more than 20-30,000 pounds) are exported to Europe by Fine Organics Division of Hexel Corporation, and White Chemical Company. The total amount of PBB exported in 1976 was approximately 805,000 pounds.

4.3 TRANSPORTATION AND HANDLING

The major exporter of polybrominated biphenyl reports that the material is shipped to Europe via water carrier. It is transported in 100 pound, polyethylene lined, fiber drums.

TABLE 4-1. POTENTIAL SOURCES OF PBB IMPORTS TO THE U.S.

COMPANY & SITE	PBB PRODUCTION STATUS	EXPORTS TO U.S.	COMMENTS
F.W. Berk Co. England	None	none	confirmed
Kalk A.G. Cologne-Kalk Germany	hexabromobiphenyl octabromobiphenyl	none	confirmed
Bolchem Dead Sea Bromine Group The Hague, Holland (U.S. Office: 415 Madison Ave., New York, N.Y.)	none	none	confirmed

SECTION V. SUMMARY OF CHEMICAL LOSSES

5.1 AIR EMISSION FROM MANUFACTURING PLANTS, PROCESSING PLANTS AND OTHER USERS

The vapor pressure of polybrominated biphenyls is very low. Exposure of this class of materials at room temperature to the atmosphere results in vaporization in quantities too small to be measured by current analytical techniques (see Table 3-3).

The processes currently in use for the manufacture of octa- and decabrominated biphenyls show that off-gases from the reactor pass through a series of scrubbers and condensers. This reduced the concentration of the volatile materials (bromine, hydrogen chloride, hydrogen bromide and solvent) from 0.5 lbs./hr. equivalent to less than 0.00033 lbs. per pound of product. No mention was made that these residual gases contained any measurable concentration of PBBs.

According to a spokesman for a former manufacturer of PBBs (Kerst, 1977), evidence was found that the lower brominated biphenyls in particular are carried over with the by-product HBr and remain as impurities in the recovered HBr solution. Information on the concentration is not available,but it is believed to be on the order of ppm. or ppb.

Usually, the recovered HBr is converted to bromine. Any PBB present as a contaminant in the HBr feed has been found in the recovered bromine.

The octa- and decabrominated biphenyls are insoluble in the solvent used during bromination and will be present in the reaction product as a slurry. The PBBs are recovered from this slurry by centrifugation. One of the New Jersey permit applications, (New Jersey State Department of Environmental Protection, 1977) reports that some particulate PBB is lost to the atmosphere during this step. The quantity noted in the permit is less than 0.0005 lbs. per pound of product.

Following recovery by centrifugation, the octa- or deca-bromobiphenyl is dried and then ground to a fine powder using pulverising equipment. Dust from this operation is removed in a bag type filter. Data supplied for a permit application to construct pollution control equipment in New Jersey showed that the vent air stream from the air filter on the grinder could contain 0.000625 lbs. of PBB per pound of product (New Jersey State Department of Environmental Protection, 1975).

Summarizing this information, calculations show that the maximum emission of PBBs to the atmosphere during manufacture by the U.S. producers does not exceed 1.25 pounds of PBBs as particulate matter, per 1,000,000 pounds of PBBs manufactured.

Air emissions from processing plants would be in the form of particulate matter emission occurring during the blending of PBBs with resin prior to extrusion or other polymer converting operations. No data are available on the potential emission from these sources.

No data are available on probable air emissions from plants that produced hexabromobiphenyl. This chemical has a higher vapor pressure than either the octa- or decabromobiphenyl. At 90°C it is less than 1 x 10^{-5} mm Hg, equivalent to a partial pressure of less than 1.3 x 10^{-8}. At room temperature, the partial pressure would be substantially less. Emission of this material as a vapor contaminant in vapor streams leaving scrubbers or equivalent equipment, can be calculated to be less than 1 ppb at ambient temperature.

Emissions of hexabromobiphenyl as particulate matter may be assumed to have been of the same order of magnitude as that reported by present manufacturers of octa- and decabromobiphenyls. However, no data are available concerning particulate matter emissions of hexabromobiphenyl.

5.2 SOLID WASTE DISPOSITION OF POLYBROMINATED BIPHENYLS

In an EPA (1975) report, the fate of Firemaster BP-6 in the environment was discussed. It was stated that,

> "Based on Michigan Chemical Company's knowledge of the end-use products into which the BP-6 was incorporated the major portion of these products (which have a useful life of 5 to 10 years) end up in a junk pile or buried in a sanitary land fill."

According to this report, the ultimate disposition of PBB upon burial is uncertain. It was believed by Michigan Chemical that the hexabromobiphenyl eventually underwent oxidative/biological degradation, forming CO_2, water, and bromide ion. Degradation proceeds more rapidly when a chemical change in the PBB molecule occurs.

The quantity of BP-6 incorporated into plastic products during the period 1970-1974 is given in Table 1-1 as 11,800,000 lbs. During the next 5 to 10 years (the useful life of plastic products) it can be expected that this amount of BP-6 will be disposed in landfills or by incineration. The probability of leaching PBB from discarded plastic products was discussed in section 1.1.3. It was concluded that leaching of PBB from discarded plastics materials was non-detectable. Leaching could occur if the plastic was eroded, exposing the PBB particle to the action of water.

Other studies noted in paragraph 1.1.3 reported that leaching of solid PBB, not mixed or coated with polymer, could be found in leaching waters to the extent of 0.1 to 0.2 ppb and in sediment samples where concentrations as high as 1.2 ppm were found. These studies were made on landfills used for disposal of manufacturing wastes.

Leachate from landfills in which BP-6 flame retardant formulated plastics products were disposed would have markedly lower amounts of PBB and in most cases would probably be non-detectable.

Solid waste material containing PBBs may be obtained from current manufacturing practice as the residue from the recovery of the solvent used in the reaction.

The only information on the amount of solid waste resulting at a manufacturing site is that reported by Michigan Chemical Co. for their former hexabromobiphenyl production operation (Kerst, 1976). This was stated to be 0.05 lbs/lb hexabromobiphenyl produced.

No other information is available concerning the quantity of PBB contained in solid waste.

It has been reported that any solid or semi-solid wastes from the production of octa- and decabromobiphenyl are put into drums and removed by a solid-waste disposal firm. Ultimate disposal methods are not known, but it is believed that the drums are buried in a chemical waste disposal pit. Michigan Chemical sent their solid wastes both to landfills and to a chemical disposal service. There are no reports that deep well disposal or off-shore disposal methods are used for solid wastes from PBB manufacturing processes.

5.3 LIQUID EFFLUENT EMISSIONS

The polybrominated biphenyls are solid at ambient temperatures. To some extent, PBBs are soluble in various solvents. Liquid losses can occur if these solutions are severed; however, according to current PBB producers, all solvent streams are collected and the solvents recovered. Disposal residues from the recovery systems have been discussed in Section 5.2 above.

By-products, or lower brominated biphenyls that may be present in the recovered solvent stream, are recycled to the process. They can also be present in the residue from the distillation recovery of the solvents. These by-products are considered waste materials and will, most probably, be sent to a chemical disposal area. The producing companies did not discuss this portion of their process.

A study of waste water samples at Dow Chemical's plant in Midland, Michigan (June 1976) by Mr. Tom Wilcox of the Michigan Department of Natural Resources showed the presence of PBBs in various waste locations in concentrations ranging from less than 0.1 ppb to less than 10 ppb. The source of the PBBs was attributed to their formation as a result of diphenyl impurities present in diphenyl oxide used to produce decabromodiphenyloxide (DBDPO).

Mr. Wilcox was also contacted concerning the actual levels of PBB reported. The use of the expression "less than" represented the limit of sensitivity of the test method. He reported that no PBB was detectable in the effluents checked at the Dow plant.

5.4 GENERAL ENVIRONMENTAL POLLUTION BY POLYBROMINATED BIPHENYLS

General environmental pollution by PBBs during production is most likely to occur as a result of particulate matter in vented gas streams or liquid effluents flowing into natural water bodies.

Exhaust gases leave production areas as vented material from by-product HBr scrubbers, or from the ventilation of grinding and packaging operations.

Any environmental pollution occurring during these operations is limited to dusting and resultant fall-out, in the area immediately surrounding the point of use or fallout in the area immediately surrounding the manufacturing building if a building or room exhaust ventilation system is used.

The material is generally packaged in 50 pound bags. Unless rupture occurs as the result of an accident, there is no general environmental pollution by the chemical during normal transport and storage.

The major application of PBBs is in the formulation of flame retardant plastic materials. In this area, PBBs are blended with resins in high intensity solids mixers such as Banbury mixers or extruders.

General environmental pollution resulting from this operation occurs when material is fed to the solids mixer or from the volatilisation of organic components during the high intensity mixing step.

The principal formulator of PBB containing resins has confirmed these routes of general environmental pollution (Gilligan, 1976). Air emissions were never analysed as the company believed that the temperatures needed to volatilise PBBs were not reached in the high intensity mixer.

This former consumer company also noted that solid losses could occur from spillage. This was normally swept or vacuumed and the collected dirt hauled to disposal area. The final cleanup of the floors was by hosing. A sample of the effluent from the primary and secondary waste treatment at this plant taken in May 1976 indicated a PBB concentration of 0.5 ppb.

Degradation of PBB containing plastics can occur in landfill disposal areas and can result in environmental exposure to PBB. This is a slow process which, in the opinion of producers and former producers, eventually results in oxidative-biologic degradation forming CO_2, H_2O and bromide ion. (EPA, 1975).

In studies of environmental pollution by octabrombiphenyl (OBBP) contained in end-use products, samples of polypropylene containing 5% OBBP were burned (Morris, et al., 1973). Analysis of the combustion gases showed that all of the bromine in the consumed samples was converted to HBr. Photolic studies showed that the OBBP degraded when exposed to UV radiation. Under the same conditions, chlorinated biphenyls did not degrade.

In another study on the incineration of plastic containing polybrominated biphenyls as a flame retardant, it was demonstrated that heating the plastic without combustion resulted in the expected release of non-degraded PBB. However, when combustion occurred, the PBBs were degraded to CO_2, H_2O and HBr (Benbow and Cullis, 1975).

Environmental pollution can occur as a result of accidental mishandling of the chemical, as in 1973, when Michigan Chemical Co. accidentally shipped their Firemaster BP-6 (hexabrombiphenyl) instead of magnesium oxide, to the Michigan Farm Bureau. The accident occurred as a result of a shortage of paper bags, which caused Michigan Chemical to package the two products in the same color bag. The bags were properly marked to show their chemical content. During transfer to and from warehouse areas, a fork lift operator failed to notice what he was moving, and as a result, both materials were stored in the same area. Thus, when the Michigan Farm Bureau ordered magnesium oxide, the order was filled from this mixed bag area (EPA 1975, Chemical and Engineering News, 1975).

The result of this accident was the contamination of cattle feed, and the subsequent death, or destruction of 11,000 cattle, 3,000 hogs, 1.5 million chickens, and 4.5 million eggs. In addition, 583 million tons of contaminated feed were buried (Chemical and Engineering News, 1975).

5.5 POTENTIAL FOR INADVERTANT PRODUCTION OF PBBs IN OTHER INDUSTRIAL PROCESSES AS A BY-PRODUCT

The accidental production of brominated biphenyls during the production of other brominated chemicals can occur if:

(a) Biphenyl is present as an impurity in the raw material being brominated.

(b) Biphenyl is formed as a degradation product of a complex phenyl compound.

(c) Brominated biphenyls are carried out with the by-product HBr and recovered bromine released during the production of PBB.

A previous report on the pollution potential of PBBs (EPA, 1975) discussed possible sources of their inadvertant production in connection with various water waste outfalls at the Michigan Chemical Co. plant. The potential sources given included:

(1) Recovery and reuse of PBB contaminated bromine from by-product hydrogen bromide released during the production of PBBs.

(2) The coupling of polybromobenzene molecules during the manufacture of hexabromobenzene

(3) The bromination of biphenyl that might be present in bisphenol A used in the manufacture of tetrabromobisphenol A.

In addition to these potential sources, there is the potential for the presence of biphenyl in diphenyl oxide used as the raw material to manufacture decabromodiphenyl oxide.

The subject of biphenyl as an impurity in the production of aromatic chemicals that can be brominated subsequently such as diphenyl oxide, was reviewed with manufacturers of biphenyl.

Biphenyl is manufactured by dehydrogenation of benzene or the hydrodealkylation of toluene. Both reactions occur at elevated temperatures and pressures and in the presence of specific catalysts.

The hydrodealkylation of toluene is one of several processes used commercially for the synthesis of benzene. Biphenyl and substituted biphenyls are recovered as by-products of this process. It is conceivable that benzene made by this process contains biphenyl

as an impurity on the order of fractions of a percent (Lowenheim and Moran, 1975). If biphenyl-contaminated benzene is used to produce brominated benzenes or to synthesize other aromatic chemicals that are subsequently brominated (as bisphenol A), it is possible that PBBs can be formed as an impurity on the order of ppm.

Bisphenol A is manufactured by the low temperature reaction of phenol and acetone. This material is used in the manufacture of epoxy resins and polycarbonate resins. Neither of these processes involve bromination.

Small amounts of bisphenol A are brominated to form tetrabrombisphenol A[a] used as a flame retardant in rubber and certain plastic materials.

The subject of breaking the isopropyl linkage between phenyl groups in bisphenol A under bromination conditions and the linking of the resultant phenyl groups to form a biphenyl type linkage was discussed with companies who manufacture bisphenol A. It was concluded that this would be a difficult if not impossible reaction.

It may be hypothesized that if bisphenol A, manufactured via phenol made from biphenyl contaminated benzene, is brominated to form tetrabrombisphenol A, then the biphenyl contaminant could also be brominated to form PBBs.

Two manufacturers of diphenyloxide (DPO) supplied analytical data. One company reported that the raw material used to produce DPO was USP grade phenol and their product contained no biphenyl as determined by GLC and mass spectrograph analysis. A typical specification of impurities for this company's DPO manufactured from USP grade phenol, is as follows:

Dibenzofuran	less than	40	ppm.
Phenol		40	ppm.
Methyl naphthalene	less than	5	ppm.
Naphthalene	" "	5	ppm.
Phenylphenol	" "	5	ppm.

[a]Manufactures include Great Lakes Chemical Co., White Chemical Corp. and Solutia Inc.

The second company reported that their regular production grade of DPO used for bromination contained less than 200 ppm biphenyl. This was determined using special GLC techniques, since DPO would normally mask the presence of biphenyl. The commercial grade of DPO was reported to contain up to 2,000 ppm of biphenyl.

5.6 POTENTIAL FOR INADVERTANT PRODUCTION OF PBBs IN THE ENVIRONMENT

There is no information on this subject. However, based on the process conditions for bromination, the simultaneous presence of bromine, with biphenyl, under conditions that would form a polybrominated biphenyl, is not believed to be possible. This view is particularly reinforced by the fact that neither elemental bromine nor biphenyl are normally found in the natural environment.

SECTION VI. FUTURE PROJECTIONS

The current market for PBBs is Europe, where there is continued acceptance of the use of these materials as flame retardants, based on their cost-effectiveness. However, the major U.S. exporter has suspended production of decabromobiphenyl. Further production for export is uncertain, pending the outcome of current investigations concerning PBBs. There is no U.S. market.

SECTION VII. USE ALTERNATIVE ANALYSIS

This section reviews alternative chemicals and processes which could replace polybrominated biphenyls as flame retardant additives to resins and other polymeric materials.

Interest in flame retardant additives has grown in recent years as a result of greater governmental emphasis on safety in all areas of human activity. Prior to this, major interest in flame retardants in plastics was in electrical applications of plastics, sponsored chiefly by insurance companies and Underwriters Laboratories.

Fifteen years ago, the major flame retardants included:

- Antimony Oxide
- Chlorinated hydrocarbon waxes (C_{18} to C_{30})
- Alkyl and Aryl Phosphates
- Chloroalkyl Phosphates

Brominated compounds were just being introduced.

In the intervening years, new plastics have been developed with accompanying new applications. These changes have created new requirements that could not be met completely by the few flame retardants available in 1963. Many new flame retardant chemicals have been marketed. Chlorinated and brominated aromatics have been in the forefront of this development.

As the emphasis on health safety has grown, toxicological studies have shown that some of the flame retardant products used in plastic and polymeric materials were potentially hazardous to health.

7.1 ALTERNATIVE CHEMICALS AS REPLACEMENTS TO PBBs IN EXISTING PROCESSES AND PRODUCTS

U.S. commercial sales of PBB-containing products, chiefly the hexabromobiphenyls, began about 1970 and rose rapidly till 1974. Production in the U.S. ceased in Nov., 1974 as a result of the accidental contamination of cattle feed in Michigan.

PBBs and alternative flame retardant chemicals are processed by blending them with plasticizers, other additives and the resin in standard equipment, following which the blend is extruded in the form of pellets. No basic design changes are required unless the alternative flame retardant chemical selected is a liquid. In this case small design changes in the feed and materials handling equipment will be required. Capital cost for such changes in most cases should not exceed the low tens of thousands of dollars.

Use of alternative flame retardant chemicals does not alter the general character of losses from the resin blending and pelletising processes which result from handling spills and dust.

7.2 ALTERNATIVE PROCESSES AND PRODUCTS WHICH COULD BE USED AS A REPLACEMENT FOR PBB

Many of the alternative flame retardant chemicals are halogenated aromatics. The processes for the manufacture of a number of these products are similar in many respects to those described for the bromination of biphenyl in Section 3.1.2. Thus, most of the equipment used to make PBBs can be used interchangeably for making many of the alternative chemicals.

Batch processes using corrosion resistant reactors and acid scrubbers are also used to manufacture most of the non-halogenated flame retardant chemicals. The capital required to modify a PBB plant for such uses is not excessive.

Many of the companies who produce the various flame retardant chemicals do so because these products are compatible with their marketing and product lines. The manufacture of these materials, at least for the larger companies, has probably been developed to serve as an outlet for other products (e.g. Dow produces bromine, biphenyl, diphenyl oxide, bisphenol A; FMC produces phosphoric acid; Great Lakes Chemical produces bromine) or because they are "specialists" in certain types of specialty organic syntheses (e.g. White Chemical Company and Fine Organics).

The change to producing chemicals that do not fall within the marketing or manufacturing area of a given company could represent a greater economic hardship than the capital investment to modify a given batch process.

7.3 ALTERNATIVE PRODUCTS

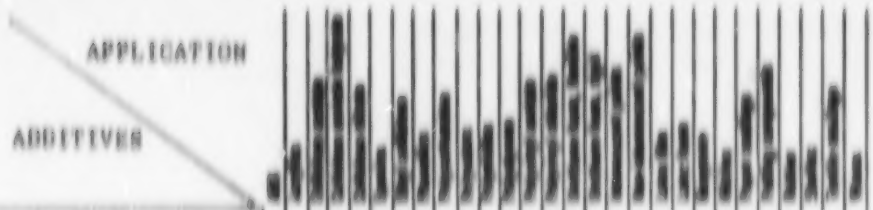
A large number of chemicals, both organic and inorganic, can provide flame retardant characteristics to all of the plastic and resin materials in commercial use. A probable reason for the development of the PBBs earlier than the decabromobiphenyl oxide is the cost of the raw material: 18¢/lb. for biphenyl vs. 60¢/lb. for biphenyl oxide (ether). There are over 50 organic-based and more than a dozen inorganic-based flame retardants available today. These chemicals, and their applications, are shown in Table 7-1.

Alternative products compete on the basis of compatibility with the plastic, effect on physical properties, price and cost-effectiveness.

An example of relative cost effectiveness is the statement that 1.4 parts of tetrabromobisphenol A (TBB-A) are required to replace 1 part of decabromobiphenyl oxide (Plastics World, 1976). On a cost-effectiveness basis, the cost to achieve equal flame retardancy is $1.22 for the TBB-A vs. $1.87 for the decabromobiphenyl oxide, per pound substituted.

Examples of the cost of some flame retardants are given in Table 7-2.

TABLE 7-1. ALTERNATIVE FLAME RETARDANT CHEMICALS AND THEIR APPLICATIONS
(Modern Plastics Encyclopedia, 1975)



Additive, organic	Trade names
Phosphate esters	Reoflex CDP Antiblaze Fyrol CEF Phosflex Kronitex
Alkyl diaryl phosphate	Santicizer 148
Cresyl diphenyl phosphate	Reoflex CDP Santicizer 140 Disflamoll DPC Phosflex 179 Phosflex CDP Kronitex CDP
Dimethyl 2-propyl 3-hydroxy butyl phosphonate	Fyrol 51
Hexabromocyclododecane	Great Lakes CD-75P Firemaster HBCD
Hexabromocyclododecene	Great Lakes CD-75
Hexabromodiphenyl	Great Lakes BP-75
Hexabromodiphenyl oxide	FR-300-BA Great Lakes DE-60
Tris (dibromochloropropyl) phosphate	Great Lakes TP-44
Octyl diphenyl phosphate	Santicizer 141 Disflamoll DPO
Pentabromoethane	FF6
Pentabromodiphenyl oxide	Firemaster BDP0-81
Trialkyl borate ester	Firemaster BP-4
Tricresyl phosphate	Reoflex TCP Liquid Phosflex 179A, B & BB TCP powder Kronitex TCP
Trixylenyl phosphate	Phosflex 4 Kronitex TXP
Tris (chloroethyl) phosphate	Reoflex TMCP Phosflex T MCP CP 160
Halogenated hydrocarbons	Firemaster LV-845T Chlorowax Chlorowax/Antimony Hexaoxide Thermogard 35
Trixylenyl phosphate	Disflamoll TXP Kronitex TXP
Triphenyl phosphate	Reoflex TPP Disflamoll TP Phosflex TPP
Trixylenyl phosphate	Kronitex TXP
Tris (isopropylphenyl) phosphate	Kronitex ITP
Phenyl isopropyl phenyl phosphate	Phosflex 510, 511 & 514

APPLICATION
ADDITIVES
Trade names

APPLICATION / ADDITIVES																													Trade names
Additives, organic (Cont'd)																													
Chlorinated paraffins (Cont'd)	X	X X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	Cl-alkane 40, 50, 60 & 70 Chlorafin (liquids & solids) Cereclors (CP series) Hüls series & Wax-CW series
Esters/ethers and oligomers of chlorinated paraffins		X X X X X						X		X	X	X	X			X X X X	X X X X	X X X X	X X X X			X		X X X	X X X	X X X	Unimol 66 & 66 Special Unimol 118 Chlorafin 71HB-64
Chlorinated hydrocarbon		X X	X X	X X		X X	X X	X X	X X	X X	X X	X X	X X	X X		X X	X X	X X	X X	X X	X X	X X	X X	X X	X X	X X	X X	Dechlo 1000 Cereclor 1370 / 170-S & 170-SV Chlorafin "HT" Chlorafin 40L
Modified carbamate																				X					X			Prem PRH
Brominated organics	X	X					X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	Firemaster 615 Firemaster BP-6 Firemaster HP-1 & BP-4 PB-100
Brominated organic salt																									X				Firemaster FF-1 & FF-2 P-56
Brominated/chlorinated organics		X									X						X	X		X			X	X	X				DCP-1010 P-1 & P-2 Firemaster 680
Blend/mix of brominated organics		X									X						X	X		X			X	X	X				Hüls 4010-00
Chlorinated organics	X					X		X	X	X	X					X		X	X				X		X				Dechlorane Plus 515 & 25 Dechlorane 602 Dechlorane 603
Chlorinated anhydride	X					X				X	X			X	X				X						X				Clorex
Chlorinated phosphate	X	X	X			X	X	X		X		X	X	X	X	X		X	X	X	X	X	X	X					Phosgard 2XC-20
Dibutyl chloroxedate		X	X	X	X		X				X		X		X											X			DBC
Dimethyl chloroxedate		X	X	X	X		X				X		X		X											X			DMC
Bromoform adduct of tri alkyl phosphate																					A				X				Pyrovatex BAC (aqueous) & Pyrovatex 1008 (solvent)
1,4,5,6,7,7-hexachloro-5-H-bis (bicycloheptene)-2,3-dicarboximide																									X				Pyrovatex N
Ethylene vinyl chloride latex		X									X				X	X	X			X	X			X	X	X			Vinnapas 2000, 4013, 8510, 4000 & 5014
Aromatic bromide						X		X	X	X		X																	Firemaster BP4
Decabromodiphenyl																													
Tetrabromophthalic anhydride											X																		
Additives, inorganic																													
Aluminum oxide tri hydrated	X	X				X		X		X	X	X		X	X		X	X	X	X	X			X	X				C-30, C-330, C-31, C-331, C-430, C-431, Hydral 705 & 710, OL-104, 107, 107-C, 431, 432, 510, 520 & 632
Ammonium bromide			X								X				X														
Ammonium fluoborate	X					X				X	X	X		X	X	X	X	X	X				X		X			
Ammonium sulfamate														X	X					X					X				

| ADDITIVES \ APPLICATION | | |

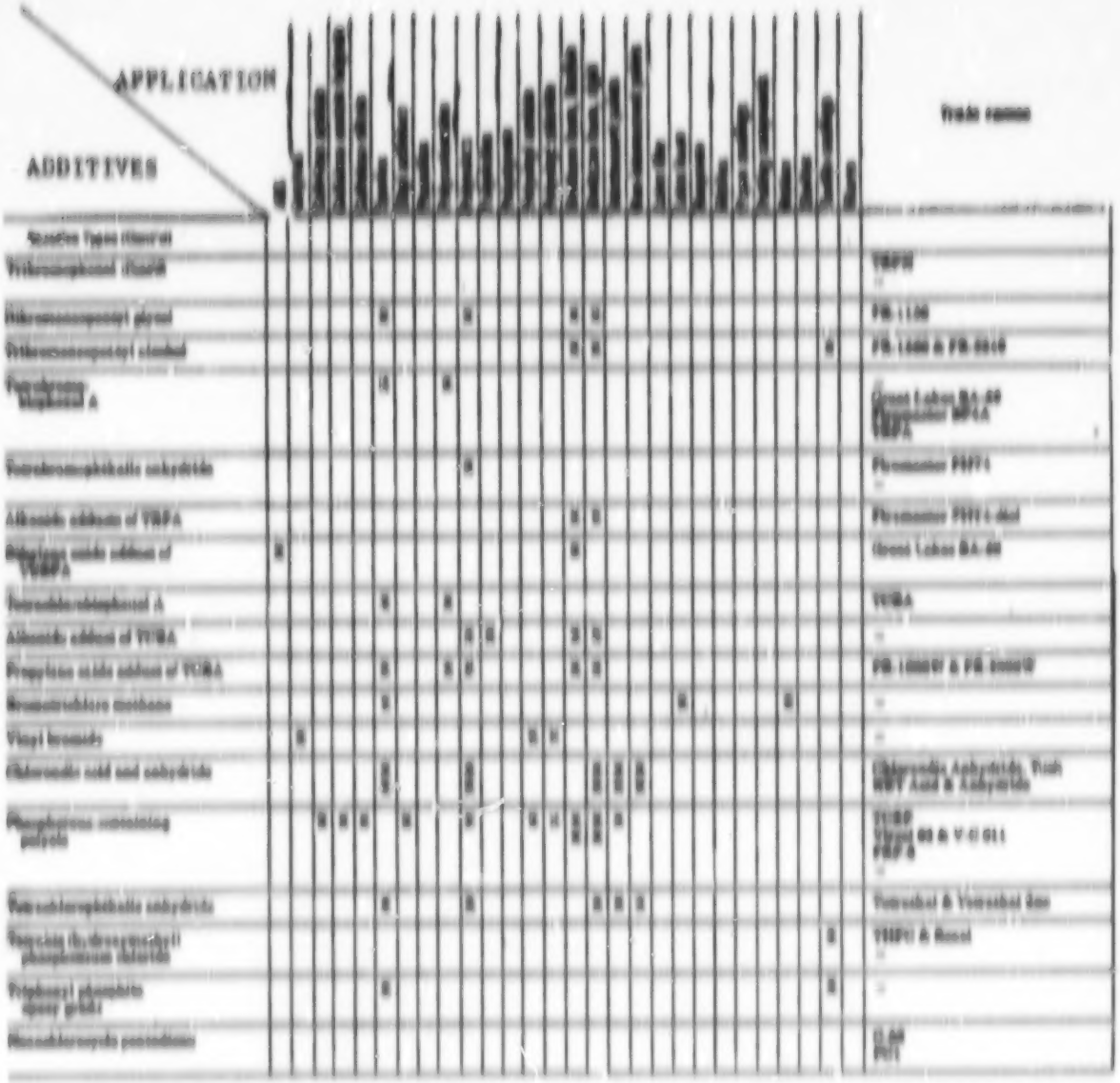


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Table 7-2 COST OF ALTERNATE FLAME RETARDANTS
(Plastics World, 1976)

Decabromobiphenyl oxide	$1.82/lb.
Tetrabromobisphenol A	0.87/lb.
Firemaster 680	1.50/lb.
Isopropylphenyldiphenylphosphate	0.70/lb.
Antimony Trioxide	1.30/lb.

Information for a full comparative analysis of all the points used to judge economic feasibility for the large number of potential alternative materials used in formulating the major flame-retarded plastics materials is not available.

7.4 ALTERNATIVE FINAL USE PRODUCTS

The final products containing flame retardant chemicals are resins that are used to produce many consumer and industrial products. The selection of a given resin is based on a combination of price and performance (physical and chemical properties).

Thus, ABS resins have high impact strength, higher tensile strengths, and higher costs when compared to a high impact polystyrene. Hence the markets for ABS resin generally are not the same as those for polystyrene.

Flame retardant plastics are selected on the basis of their ability to perform. Plastics, in general, are alternatives to older construction materials such as metal and wood. In this sense, flame retardant plastics, as end products, are, themselves, the alternative to materials formerly in use.

7.5 TRANSPORTATION AND HANDLING

Flame retardant chemicals, by their nature, are non-flammable. They are usually high boiling liquids or solids. As a class, they are non-hazardous. The materials are shipped in multi-wall paper bags, fiber or non-returnable metal drums. Normal care must be exercised in handling these materials to ensure that rupture or puncture of the containers does not occur.

Flame retardant containing resins are shipped as a finished product suitable for extrusion or molding, or as a concentrate to be blended with uncompounded resin prior to extrusion or molding. These formulated products also present no fire or vapor pressure hazard and there are no governmental regulations concerning the handling or transportation (normally by truck or rail) of the formulated resins. There are no restrictions on air or boat transport.

These materials, when packaged in standard containers, may be stored in normal storage or warehouse facilities. No unusual precautions are required. With regard to the handling of spills, if container breakage occurs, normal cleanup practice as for any spilled solid should be followed. Waste materials should be disposed of in a normal manner (to land fill).

7.6 CURRENT ENVIRONMENTAL PRACTICES

The alternative flame retardant chemicals with physical properties similar to those of the PBBs (solid, fine powder, high boiling, non-corrosive) are handled in the same manner as the PBBs.

Losses will be those expected from handling powder materials. Suitable filters are used on ventilating systems associated with grinding, blending and mixing operations. Materials reclaimed from the filters can be reused as they are not contaminated with dust or other impurities. Otherwise, together with floor sweepings, they will be drummed and sent to approved landfills.

Small users of these materials would combine the flame retardant wastes with general plant wastes.

For reuse in the process, the user (i.e., the resin compounder) seldom reclaims any solids recovered from pollution control devices. Losses of the compounded flame retardant resin resulting from scrap are seldom recovered and are usually combined with other plant wastes for general solids disposal.

Because of the high boiling point of most of the chemicals used as flame retardant additives, plastic extrusion temperatures rarely reach the point at which the additive is vaporised. In the event that such a temperature is reached, suitable ventilating equipment can be used. In most plants the exhaust air is emitted through stacks without further control.

The available data are insufficient to assess quantitatively the potential environmental contamination from these sources.

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